It is a disadvantage of said method that an alloy of aluminium metals is required, which comprises components part of which are highly precarious in environmental aspects and can only be recovered by very expensive separation techniques.

US 3,923,716 describes the preparation of aluminium acrylate in two steps. First, acrylic acid is added to aqueous sodium hydroxide to form sodium acrylate, which then is caused to react with aluminium trichloride to form (mono-, di-, tri-) aluminium acrylate and sodium chloride. Since the aluminium acrylate is poorly soluble, it can easily be separated from the dissolved sodium chloride and the aqueous reaction mixture. The disadvantage of said method, however, is the large quantity of hydrochloric acid which is dissolved in water and partially contaminated with product and needs to be disposed of.

The preparation of the corresponding salts of titanium is known from US 5,998,646. However, the continuous feeding of oxygen for the reaction and a certain degree of O_2 saturation has not been disclosed therein. On the contrary, the reaction is carried out at reduced pressure, with exclusion of air, and at elevated temperature, so that the absence of oxygen and a solvent atmosphere can be expected.

It is an object of this invention to eliminate the shortcomings described hereinabove and, in particular, to provide a method for producing solely unobjectionable by-products which can be separated easily and completely and which is useful for producing very pure carboxylic acid metal salts of various metal ions, preferably without formation of undesired polymeric compounds and without the need of additional, laborious purifying steps.

According to the present invention, the problem has been resolved by a method for preparing metal salts of unsaturated, short-chain carboxylic acids by reaction

- of metal-alcoholate compounds
- with carboxylic acids of the general formula

$$C_nH_{2n-1}C(=O)OH \ ,$$

wherein the double bond is in 2- or 3-position and
n represents 2, 3, 4, 5, or 6 and/or maleic acid (less desirable),

in the presence of oxygen, which is continuously fed so that its concentration in the reaction solution is at least 50 %, and
the metal salts have at least one group of the formula

$$C_nH_{2n-1}C(=O)O- \quad \text{and/or} \quad -OC(=O)CH=CHC(=O)O-(H)$$

and the following metals or mixtures thereof
Al, Si, Sn, La, Zr, Cu and/or Zn.

Especially the metal salts of unsaturated, short-chain carboxylic acids have the general formula

$$M(OOCC_nH_{2n-1})_a(R^1)_b$$

and can be obtained by reaction of a linear or branched, unsaturated carboxylic acid of the formula

$$C_nH_{2n-1}\text{-}COOH,$$

wherein **n** represents 2, 3, 4, 5, or 6 with the double bond in 2- or 3-position, preferably in 2-position, with a metal compound of the general formula

$$M(R^1)_c$$

and, optionally, among others

$$H(R^1)\ ,$$

wherein

a is at least 1,

b is 0, 1, 2 or 3 and

(a+b) and **c** are independently of one another an integer of 2 to 4,

M is Al, Si, Sn, La, Zr, Cu, or Zn, particularly Al or Zr,

$\mathbf{R^1}$ represents an alcoholate group having a C_1- to C_6 hydrocarbons residue, wherein $\mathbf{R^1}$ is a saturated, linear or branched alcoholate group, which can be obtained from an alcohol having at least one -OH group, wherein the -OH groups are preferably primary and/or secondary -OH groups,

or

$$R^2-\overset{\text{O-}}{\overset{|}{C}}=CH\text{-}C(=O)O\text{-}R^3 \quad ,$$

wherein $\mathbf{R^2}$ or $\mathbf{R^3}$ represent $-CH_3$, $-C_2H_5$, $-C_3H_7$ or $-C_4H_9$ and **n**, $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ may be different for each **a**, **b**, and **c** and at least one $\mathbf{R^1}$ in $\mathbf{M(R^1)_c}$ represents an alcoholate group having a C_1 - to C_6 hydrocarbons residue, in the presence of oxygen (O_2), which is continuously fed so that its concentration in the reaction solution is at least 50 %.

The preferred embodiments of the subject invention are set out in the additional independent claim 2, the subordinate claims, or are described hereinbelow.

According to the present invention, the reaction is carried out in the presence of oxygen so that the reaction solution contains at least 50% oxygen, preferably at least 90%, for example by feeding a gas mixture containing 5 to 30 vol% oxygen, preferably 15 to 25

- defoamer or defoaming products
- for producing and/or modifying inorganic products which may contain functional groups
- for producing and modifying ceramics.

Examples

Preparation of Liquid Metal Salts of Unsaturated Carboxylic Acids

The experiments were carried out in a 500-ml reaction flask made of glass and equipped with thermometer, stillhead, dropping funnel, stirrer, and gas supply. The first experiment was carried out under a nitrogen blanket, the second with compressed-air passage. The reaction heat was removed by water-bath cooling. The oxygen content in the gas used in the examples 2 to 7 was from 15 to 30 vol% (average 21 vol%). In the examples 8 to 10 the reaction mixture was saturated with oxygen.

Example 1 Preparation of aluminium tri-acrylate in solution (Comparative Example)

Into the flask described hereinabove there were placed 123.1 g of aluminium-tri-sec-butanolate, 119.9 g of diethylene glycol monobutyl ether, 0.7 g of 4-methoxyphenol, and 2 g of copper chips. To this mixture there were added in drops 108 grams of acrylic acid by means of a dropping funnel. The acid was added at room temperature (25 °C) during 1 hour and 4 minutes. Owing to the reaction heat, the temperature increased to 36 °C. The mixture was cooled to 25 °C using a water bath and stirred for 23 minutes after which time the temperature increased again and the product gelled. Undesirably, the product polymerized, although polymerization inhibitors, such as copper chips and 4-methoxyphenol had been added during the reaction.

Example 2 Preparation of aluminium tri-acrylate in solution

Into the flask described hereinabove there were placed 102.1 g of aluminium tri-isopropanolate, 120.1 g of diethylene glycol monobutyl ether, and 0.7 g of 4-methoxyphenol. To this mixture there were added in drops using a dropping funnel 108 grams of acrylic acid. The acid was added during 15 minutes at room temperature (25 °C). Owing to the reaction heat, the temperature increased to 53 °C. The mixture was cooled to 39 °C using a water bath. The

Example 6 Preparation of titanium tetra-acrylate in solution (not according to the invention)

Into the flask described hereinabove there were placed 510.6 g of titanium-tetra-butanolate, 498.6 g of diethylene glycol monobutyl ether, and 2.8 g of 4-methoxyphenol. To this mixture there were quickly added in drops 432.6 grams of acrylic acid by means of a dropping funnel. The temperature thereby increased to 50 °C. The product remained liquid and stable so that it could be heated to 90 °C during 30 minutes. The co-product butanol was expelled during 1 hour using vacuum up to 200 mbar.

Example 7 Preparation of magnesium di-acrylate in solution (not according to the invention)

Into the flask described hereinabove there were placed 510.55 g of magnesium di-butanolate, 498.6 g of diethylene glycol monobutyl ether, and 2.8 g of 4-methoxyphenol. To this mixture there were quickly added in drops 431.7 grams of acrylic acid by means of a dropping funnel. The temperature thereby increased to 48 °C. The product remained liquid and stable so that it could be heated to 90 °C during 30 minutes. The co-product butanol was expelled during 1 hour using vacuum up to 200 mbar.

Preparation of Solid Metal Salts of Unsaturated Carboxylic Acids

Additional experiments were carried out for preparing solid metal compounds of unsaturated carboxylic acids.

General Prodecure / Equipment

The experiments were carried out in a 1,000-ml reaction flask made of glass and equipped with a rotary evaporator and vacuum pump. At a vacuum of 750 mbar the acrylic acid was sucked into the flask through a glass tube.

Example 8 Preparation of solventless aluminium tri-acrylate

Into the flask described hereinabove there were placed 204.2 grams of aluminium tri-isopropanolate to which 216 grams of acrylic acid were added during 8 minutes at room temperature (25 °C). The procedure was as set forth hereinabove. Owing to the reaction heat, the temperature increased to 32 °C. The resultant product was a white, solid substance. The rotary evaporator heating then was switched on and gradually heated to 70 °C. At the same time the vacuum was gradually adjusted to 24 mbar. The isopropanol was thereby expelled yielding a white powder.

Formulation 3

Formulation 3 is comprised 31 % aluminium tri-acrylate, 45 % n-butylacrylate, and 24 % 2-propanol. The resultant liquid was clear and slightly viscous.

Formulation 4

Formulation 4 is comprised of 30 % aluminium tri-acrylate, 32 % 2-hydroxyethylmethacrylate, and 38 % 2-butanol. The resultant liquid was clear and slightly viscous.

Formulation 5

Formulation 5 is comprised of 35 % aluminium tri-methacrylate, 43 % n-butylacrylate, and 22 % 2-propanol. The resultant liquid was clear and slightly viscous.

Formulation 6

Formulation 6 is comprised of 21 % aluminium tri-acrylate, 31 % n-butylacrylate, and 48 % hydroxyethylmethacrylate. The resultant liquid was clear and slightly viscous.

Formulation 7 (not according to the invention)

Formulation 7 is comprised of 90 % Formulation 3 and 10 % *tetra*-n-butyl zirconate. The resultant liquid was clear and slightly viscous.

Formulation 8 (not according to the invention)

Formulation 8 is comprised of 70 % Formulation 3 and 30 % *tetra*-n-butyl zirconate. The resultant liquid was clear and slightly viscous.

Formulation 9 (not according to the invention)

Formulation 9 is comprised of 90 % Formulation 3 and 10 % *tetra*-n-butyl titanate. The resultant liquid was clear, slightly yellowish, slightly viscous.

Formulation 10 (not according to the invention)

Formulation 10 is comprised of 70 % Formulation 3 and 30 % *tetra*-n-butyl titanate. The resultant liquid was clear, slightly yellowish, slightly viscous.

All of the formulations 1 to 10 also contain 3 wt.% photoinitiator (2,2-diethoxyacetophenone) and approx. 0.15-0.2 wt.% stabilizer (4-methoxy-phenol).